SUBSTITUENT EFFECTS ON C-H BOND STRENGTHS OF THE BENZYLIC POSITIONS IN COAL-MODEL COMPOUNDS: EFFECTS OF SULFUR, OXYGEN, NITROGEN AND AROMATIC MOIETIES ON THE STABILITIES OF RADICALS.

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Abstract: Incorporation of equilibrium acidities of week acids (A-H) and the oxidation potentials of their conjugate bases (A') in a thermochemical cycle enable accurate determination of the effects of substituents on bond dissociation energies (BDEs) of the adjacent C-H bonds. Substraction of these (BDEs) from the BDE of methane provided a measure of the radical stabilization energies (RSEs) for the corresponding radicals relative to that of methyl radical. In this study, we have examined the effects of sulfur, oxygen, nitrogen, aromatic and coal-model structures on RSEs in RX(CH·A, where the acceptor function (A) is phenyl, fluorenyl and PhC(O). For the heteroatom substituents with A equal to PhC(O), RSEs follow the trend: N > S = O). Substitution of phenyl group stabilizes the adjacent carbon radical by 10.5 kcal/mole (referred to hereafter as kcal). Naphthyl, phenanthrenyl, and 9-anthracenyl substituents provided less stabilization to the radical center than a phenyl group. Explanations are given for the difference in stabilities of these radicals and of other types of radicals studied.

Introduction: The effects of electron donors and electron acceptors on the stability of an attached carbon radical center have been well recognized. The electron donor and acceptor groups often stabilize the radical to an extent greater than would be expected on the basis of the individual contributions of both substituents. 4-8 The terms push-pull resonance, merostabilization, and captodative have been used to describe the extra stabilization that results from the presence of both donor and acceptor groups. Kinetic data and theoretical calculations have been used to support as well as deny the existence of substituent effects on radical stabilities. 1-10 Viehe and his co-workers have concluded on the basis of electron spin resonance data and qualitative theoretical interpretation that the effects are always synergistic. However, the recent results of theoretical calculations by Pasto cast doubt on the existence of the captodative phenomenon and suggest that the effects will vary depending on the nature of the donors and acceptors.

The discrepancies outlined above demonstrate the difficulties in obtaining BDEs and in establishing the existence of synergistic stabilization that results from the interactions between the unpaired electron of the radical and the adjacent substituents. The measurement of homolytic bond dissociation energies have been proven to be difficult^{11,12} even in the simplest of molecules.¹³⁻¹⁵ The values of the C-H bond strengths of labile systems are even more scarce. For example, the homolytic bond dissociation energies and the thermochemistry associated with labile high molecular weight hydrocarbons and sulfur-containing organic structures important to coal are lacking because these systems are inappropriate for the most common gas-phase techniques.

Recently, we have used an electrochemical method $^{16-20}$ to estimate BDEs of the acidic H-A bonds in weak acids (eq. 1).

BDE =
$$1.37pK_{HA}$$
 + $23.1E_{ox}(A^{-})$ + 73.3 (1)

The method requires that the acids be strong enough to allow acidity measurements to be made in DMSO solution. Equation (1) is based on a thermochemical cycle^{17,18} in which the factors $\bf 1.37$ and $\bf 23.1$ are used to convert pK $_{\rm H-A}$ units and oxidation potential (eV) units to kcal/mol. The constant

73.3, relates the free energies in solution to gas-phase ΔH° values, and is made up of the free energies of formation $(\Delta G^\circ_{\ t})$ and solvation $(\Delta G^\circ_{\ t})$ of the hydrogen atom, the free energy of proton transfer $(\Delta G^\circ_{\ t})$ from water to DMSO, and TaS for the reaction of RH ---> R^+ + H^-. The oxidation potential values of the conjugate bases (A°) are obtained from cyclic voltammetric measurements in dilute DMSO relative to ferrocene/ferrocenium ion. This electrochemical method is very powerful as it provides BDEs for large numbers of compounds that otherwise would be difficult or impossible to obtain. Also, the effects of electron donor (D) and acceptor (A) groups attached to a radical center can now be accurately determined. The experimental conditions used are very mild so that the BDEs of acidic C-H bonds of thermally labile molecules can be easily estimated.

In this paper we have obtained quantitative experimental estimates of the size of radical stabilization energies (RSEs) of radicals of the type $D^-(CH^{\scriptscriptstyle \circ})-A$ and $D_2^-(C^{\scriptscriptstyle \circ})-A$ from the homolytic bond dissociation energies of the C-H bonds in α -substituted acetophenones by using eq. 1. These BDEs provide good estimates of the RSEs, relative to the stability of the methyl radical (BDE of C-H in CH $_{\!\!4}$ is 105 kcal). The example, the BDEs of the acidic C-H bond in PhCOCH $_{\!\!4}$ Me and PhCOCH $_{\!\!4}$ OMe are 88 and 81 kcal respectively, and that of the acidic C-H bond in acetophenone is 93 kcal. Therefore, the RSE of the PhCOCH $_{\!\!4}(\cdot)$ radical is estimated to be 12 kcal, and the RSEs estimated for PhCOCH(\cdot)Me and PhCOCH(\cdot)OMe radicals are 17 and 24 kcal respectively. This means that the presence of the methyl and methoxy groups has increased the stability of the PhCOCH $_{\!\!4}(\cdot)$ radical by 5 and 12 kcal respectively. We have also examined the effects of aromatics, sulfur and other heteroatoms on the donor-CH-acceptor type radicals and have found that, for sulfur functions, the RSEs increased progressively as the acceptors changed along the series: Ph, fluorene and PhCO. Most of the polyaromatic substituents were studied with the acceptor being PhCO. The RSE reached the minimum when the α -substituent was 9-anthracenyl system, presumably due to the large steric inhibition.

Results and Discussion: The radical stabilization energies (RSEs)²¹ of carbon-centered radicals attached to sulfur, oxygen and nitrogen groups are presented in Table I. Our study of the effects of heteroatom substitution on homolytic bond dissociation energies provides new bond strengths and new insights into structural features controlling stabilization energies.

RSEs for PhCH(·)-SPh. Examination of the data in Table I (entry 2) shows that the BDE of the acidic C-H in PhCH₂-SPh is 84 kcal. This value was estimated by the combination of the pK_{HA} of PhCH₂-SPh and the E_{OX} of the conjugate base using eq. 1. Comparison with the known BDE value for toluene (88), leads to 4 kcal extra stabilization relative to the PhCH₂(·), or 21 kcal compared to the CH₃(·) radical. The sum of the RSEs for the PhSCH₂(·) radical (12 kcal, 105 -93) and PhCH₂(·) radical (17 kcal, 105 - 88) is 8 kcal larger than the RSE of PhCH(·)-SPh (29 vs. 21 respectively).

RSE for 9-PhS-Fl(·). Entry 5 of table I shows that the PhS group has a larger radical-stabilizing effect (2 extra kcal) on the fluorenyl radical (Fl·) than on the benzyl radical (compare entries 2 and 5). It is surprising to observe such behavior since Fl· is supposed to be stabilized more than benzyl radical by delocalization. Because of this inherent stabilization of Fl· radical, one would expect that the stabilizing power of the sulfur atom be less in the fluorenyl system than in the benzyl system. The extra stabilization of the PhS-substituted Fl· may be explained by virtue of contributor I.

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RSEs for PhS-CH(·)COPh: The BDE of the C-H bond in PhS-CH2COPh is 81.5 kcal. The RSE for the corresponding

radical is 23.5 kcal relative to $CH_3(\cdot)$ radical. The value of 23.5 kcal is 0.5 kcal lower than the combined RSEs for $PhSCH_2(\cdot)$ and (\cdot) CH_2COPh radicals (24 kcal, 12 + 12). Table I shows clearly that RSEs for sulfur containing radicals increase progressively as the acceptors change along the series: Ph, fluorene (Fl), and COPh with the latter being the most stabilizing acceptor (12 kcal relative to acetophenone). The special electronic effects of the carbonyl in combination with the sulfur substituents is probably due to the conjugative and electrostatic interactions between the negatively charged oxygen and the positively charged sulfur (II). However, the RSEs of $PhSCH(\cdot)$ -A radicals are always smaller than the sum of the RSEs estimated from the individual radicals $\{PhSCH_1(\cdot)\}$ and $\{PhSCH_2(\cdot)\}$ and $\{PhSCH_3(\cdot)\}$ and $\{P$

PhSCH(-)-COPh ----> PhSCH(·)COPh <---> PhS**CH = CO(*)Ph

The effect of a second PhS substitution into already doubly substituted methane (entries 3, and 9) is negligible. The small decrease in BDE compares well with the third phenyl substitution into methane ($\Delta BDE = 1$ kcal) and is probably due to a large steric effect. 11,16

Also from Table I, it is evident that the alkyl or aryl groups attached to the sulfur are not exerting any appreciable effects on the radical center connected to the sulfur atom (compare entries 5 & 6, and 8 & 10). The sulfur atom appears to act as an insulator thereby preventing the conjugation between the radical center and the group attached to the sulfur donor.

RSEs for MeO-CH(·)COPh and c-C,H $_1$ oNCH(·)COPh: The acidic C-H bonds in MeOCH $_2$ COPh and c-C,H $_1$ oNCH $_2$ COPh are 81 and 72 kcal respectively, giving RSEs of 24 and 33 kcal (Table I, entry 11 and 12). The RSEs for the corresponding radicals are equal to the sum of the RSEs of the individual radicals, indicating the apparent absence of synergism in the systems studied.

α-Substituent effects on BDEs of the α-C-H bond in acetophenone: In table I we saw that the introduction of phenylthio group into the α-position of acetophenone causes a 11.5 kcal increase in RSE of $PhCOCH_2(\cdot)$ radical. However, in table II (entries 2-6) we see that the introduction of a phenyl, naphthyl, phenanthrenyl, or anthracenyl substituent causes a smaller increase in RSE. The 9-anthracenyl substituent (entry 7) gave the smallest increase probably because of the greater steric and stereoelectronic demands of the 9-anthracenyl than the PhS and the other aryl groups. Furthermore, the role of a polar contributor must be larger for the PhS to show greater ability than the aryl groups in stabilizing the phenylacetyl radical. For example, contributor (III) dominates over contributor (IV) due to the electrostatic interaction between the sulfur and the oxygen atoms. The Ph group is less effective in this delocalization because contributor (IV) is higher in energy due to the loss of aromaticity of the phenyl ring. Substitution of an α-hydrogen in acetophenone by a pyrenyl group lowers the BDE of the α-C-H bond by 12.5 kcal (entry 8). This increase in RSE, compared to the other aromatic systems, is attributed to the delocalization of the unpaired electron into the larger pyrenyl moiety, an effect comparable in magnitude to that of aryl methyl radicals. **

Phs-CH(·)-COPh <----> Phs·-CH = CO(·) Ph
(III)

Ph-CH(·)-COPh <----> Ph·-CH = CO(·) Ph

Remote substituent effects on BDEs of the α -C-H bond in ketones: The BDEs of acetone, acetophenone, p-methyl-, p-methoxy-, p-cyano-acetophenone are also presented in table II. Examination of entries 9-13 show that remote electron donating and electron accepting groups make the

ketone less or more acidic, but have no effect on BDE's of the $\alpha\text{-C-H}$ bonds. The changes in acidities of the ketones are offset in eq.1 by shifts of $E_{ox}\left(A^{-}\right)$ to less or more positive potentials. The result is no change in BDE. This observation indicates that the remote substituent is not interacting directly with the incipient radical to provide additional stabilization.

Chromium tricarbonyl effect on BDE of the $\alpha\text{-C-H}$ bond in phenylacetophenone: We have shown so far the effectiveness of eq.1 in estimating the BDEs of the acidic α -C-H bonds in substituted acetophenones. We now extend our studies to chromium tricarbonyl complex of α -phenylacetophenone. The $\pi\text{-coordination}$ of Cr(CO), to benzene ring attached to the $\alpha\text{-position}$ is conclusive based on the NMR data. Our objective here is to obtain the first quantitative information concerning the effect of transition metal complexes on the PKAH values and BDEs of the acidic C-H bonds. Entry 14 of table II shows that $Cr(CO)_3$ group increases the acidity of the $\alpha\text{-C-H}$ bond by 4.7 pK units (6.3 kcal; compare entries 2 & 14). T large increase is probably due to the field and inductive effects of the three carbonyl groups attached to the chromium Similar acidity effects were observed when Cr(CO), was π-coordinated to benzoic and phenylacetic acids.25 The oxidation potential of the complex anion is less negative than that of the parent compound giving once again no net change in BDE

Conclusion: Homolytic bond dissociation energies in DMSO for $\alpha\text{-C-H}$ bonds in aryl, sulfur-, oxygen-, and nitrogen-containing compounds have been measured using pK_{RA} and $E_{ox}(A^{-})$ data in eq In every case, the radical stabilization energies (RSEs) of RXCH(\cdot)-A are always equal or smaller than the sum of RSEs of the two radicals. The increase in RSEs for sulfur group along the series: Ph, Fl, and COPh, is in correspondence with the ability of the acceptor to stabilize the negative charge on carbon for contributor of the type PhS*-CH = CO(-) Ph. Remote electron withdrawing, electron accepting and Cr(CO) groups have little or no effects on BDEs of the acidic α -C-H bonds indicating that these groups do not interact directly with the unpaired electron situated on the carbon radical center.

References and Notes:

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- 2. Same as in 1.
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 The radical stabilization energies are defined as RSE = $\triangle BDE = BDE(A-CH_2-H) - BDE(A-CH_2-D)$, where A and D are the acceptors and the donors respectively.
- The BDE of $\text{CH}_3\text{-H}$ = 105 kcal³. The RSE of PhCH(·)-SPh relative to methyl radical is 21 kcal (105 84).
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Table I. Acidities and Bond Dissociation Energies (BDEs) for the α -C-H Bonds in Heteroatom-Containing Systems.

	Entry	Substrates	pK _{HA} a	E _{OX} (A-) b	BDEc	RSE ⁹		
	1.	PhCH2-H			88 ^d	0.0		
	2.	PhCH ₂ -SPh	30.8	-1.353	84	4		
	3.	PhCH (SPH) 2	23.0	-1.000	82	6		
	4.	H-FL-H	22.6	-1.064	80	0.0		
	5.	9-PhS-FL-H	15.1	-0.860	74 ^e	6		
	6.	9-MeS-FL-H	18.0	-1.015	74.5	5.5		
	7.	H-CH ₂ COPh	24.7	-0.607	93	0.0		
	8.	PhS-CH ₂ COPh	17.1	-0.660	81.5 ^f	11.5		
	9.	(PhS) ₂ -CHCOPh	12.0	-0.370	81	12		
	10.	PrS-CH₂COPh	19.9	-0.850	81	12		
	11.	MeO-CH₂COPh	22.9	-1.030	81	12		
	12.	$C-C_5H_{10}NCH_2COPh$	23.5	-1.439	72	21		

"Measured in DMSO against two indicators. "In volts; irreversible oxidation potentials (E_p) measured in DMSO by cyclic voltammetry and referenced to the ferrocene/ferrocenium couple. Calculated(in kcal/mol)using eq 1. Radical stabilization energy (RSE = 17 kcal/mol) relative to CH3-H (BDE = 105 kcal/mol). *Relative to H-FL-H(BDE = 80 kcal). to $PhCOCH_2-H(BDE = 93 kcal)$. $^{9}RSE = \Delta BDE$.

Table II. Acidities and Bond Dissociation Energies (BDEs) for the α -C-H Bonds in Ketones.

Entry	Substrates	pK _{HA} a	$E_{OX}(A^{-})^{b}$	BDEc	RSE ^f				
=====		=========							
1.	PhCOCH₃	24.7	-0.607	93	0.0				
2.	PhCOCH₂Ph	17.7	-0.650	82.5	10.5				
3.	PhCOCH₂Naph-1	17.6	-0.626	83	10.0				
4.	PhCOCH₂Phen-3	17.2	-0.576	83.5	9.5				
5.	PhCOCH₂Phen-9	17.5	-0.597	83.5	9.5				
6.	PhCOCH ₂ Anth-1	17.2	-0.625	82.5	10.5				
7.	PhCOCH ₂ Ant h - 9	18.9	-0.63 5	84.5	8.5				
8.	PhCOCH ₂ Py-1	15.7	-0.618	80.5	12.5				
9.	CH,COCH,	26.5	-0.674	94	0.0				
10.	PhCOCH,	24.7	-0.607	93 ^d	1.0				
11.	p-MePhCOCH,	25.0	-0.597	94	0.0				
12.	p-MeOPhCOCH ₃	25.7	-0.657	93	1.0				
13.	p-CNPhCOCH ₃	22.0	-0.436	93	1.0				
14.	PhCOCH ₂ Ph								
	ħCr(CO) ₃	13.1	-0.377	82.5	10.5				

For a, b, and See footnotes in table I. Relative to acetone (BDE = 94 kcal). Relative to PhCOCH₂-H (BDE = 93 kcal). Radical stabilization energy (RSE).